

Preparation of Nickel Catalysts Deposited on Gamma Alumina to Process Hydrodeoxygenation First Generation Biodiesel

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ABSTRACT

Due to the current problems in the consumption of fossil fuels nowadays; by the wet impregnation method incipient, a nickel catalyst supported on gamma alumina was prepared using as precursor salt Nickel acetate tetrahydrate, because the precursor salt is not soluble in water, a variant of the method, consisting of a grinding and physical blending of boehmite precursor to nickel salt, once the homogeneous physical mixture drops of a solution of nitric acid dissolved 1:16 in water was added, was applied in this possible to modify the pH of the boehmite surface and achieve the impregnation of the salt. They were anchored nickel particles by a controlled, to obtain nickel oxide, calcination method finally the metal oxide catalysts were reduced by exposure to a flow of hydrogen at 400 ° C, obtaining as a product catalyst Ni/ γ -Al₂O₃ can accelerate and direct the hydrodeoxygenation reaction of oxygenated organic compounds for converting a first generation biodiesel second generation biodiesel.

Keywords: Ni/ γ -Al₂O₃; second generation biodiesel, oxygenated organic compounds.



1. Introduction

At present about 80% of world energy demand is obtained by burning fossil fuels. This leads to a depletion of fossil energy resources, which are limited, which has led to the use of fossil fuels is identified as the main cause of global climate change due to emission of pollutants as a result of combustion.

One option to reduce the consumption of fossil fuels and their impact on the environment is the use of renewable energy based on biomass processing, because they have a huge energy potential, and can contribute to the reduction of emissions of greenhouse emissions. Such is the case of Biodiesel.

The method of application of biodiesel and its blends with diesel fuel based oil can be used in diesel engines without any significant engine modification [1].

The disadvantages encountered in the application of first generation biodiesel have attracted interest for the development of catalytic hydrogenation processes of methyl esters from vegetable oils and animal fats, so that they can transform a condition of polyunsaturated to monounsaturated. This new biodiesel is what is known as second generation biodiesel.

In recent years, strategies have been developed for the catalytic production of second generation biodiesel from oils and fats. These processes reacted oils, fats and first generation biodiesel at elevated temperatures in the presence of a heterogeneous catalyst and hydrogen injection, which is achieved with oxygen can be separated through the formation of oxygenated functionalities groups, among which we mention H_2O , CO_2 and CO , such reactions are known as hydrodeoxygenation reactions (HDO) [2].

With the results of performance characterization of catalysts and reaction conditions most suitable catalysts preparation, and the conditions of temperature and hydrogen pressure submit higher reaction yield (HDO).

2. Experimental

- The necessary amounts of boehmite and acetate tetrahydrate $Ni (C_2H_3O_2)_2 \cdot 4H_2O$, in order to obtain the percentages of active metal phase sought (3%, 5% and 7%) are weighed.
- A physical mixing of the catalyst support and the precursor salt is performed by applying a fine grinding process, mixed quantities of boehmite and acetate tetrahydrate $Ni (C_2H_3O_2)_2 \cdot 4H_2O$.
- A solution volume ratio of 1:16 (water:acid) Nitric acid is prepared.
- Once you have the powder catalyst support precursor salt and thoroughly mixed, begin to incorporate drip solution of nitric acid, until a smooth paste.
- The paste was allowed to dry at room temperature for 48 hours.
- Once dry the paste extrusion process is performed to obtain pellets cut to the same size, making sure not pulverized, because if so, the catalyst could be recovered after hydrodeoxygenation process.



- Subsequently all mixtures into pellets were calcined at 510 ° C in the presence of oxygen. The purpose of the catalyst is to calcine the removal of water from the boehmite and obtain γ -Al₂O₃, and moreover, burn acetylacetonate and nitric acid to obtain the end oxides of Nickel on γ -Al₂O₃ deposited.

3. Results and discussion

Characterization of catalysts Ni/ γ -Al₂O₃ with 3%, 5% and 7% by weight of active phase was performed by Raman spectroscopy, X-ray diffraction, scanning electron microscopy and EDS. Then the results of the characterization and the interpretation and discussion of the results obtained by each technique is.

Figure 1 shows Raman spectra which were used to monitor the preparation process of the catalysts of Nickel γ -Al₂O₃, in the blue spectrum of the precursor salt of Nickel (Nickel acetate tetrahydrate Ni (C₂H₃O₂)₂·4H₂O, NIAC4H₂O) occurs are shown. Can also be observed in the Raman spectrum green mix in coordination (NIAC4H₂O + Boehmite = PTACABO5), where you can observe the characteristic Raman shift of the prepared mixture to obtain a 5 wt% Nickel on gamma alumina, which is apparent that the process of deposition of the precursor salt by the wet impregnation method was incipient adequate, and pH modification helped the impregnation of salt, with a new mix in coordination was obtained with very different peaks which presents the single precursor salt. It also shows clearly that the catalyst of Nickel oxide on gamma alumina ONIGA5 (preparation to obtain 5% by weight of Ni) no characteristic peaks in Raman shift, this is because it is very small amount of Nickel oxide deposited on bracket. But it was also demonstrated that the process of calcination at 510 ° C is suitable because the characteristic peaks disappeared from the organic components of the mixture in coordination. Finally, the spectrum of the catalyst over 5% by weight of Nickel on gamma alumina (ONIGA5) which was reduced to 400 ° C and a pressure of 20 bar of hydrogen, which is observed that there are no peaks characteristic Raman occurs, this is because Raman metals detected at baseline, regardless of the percentage of metal containing the substance.



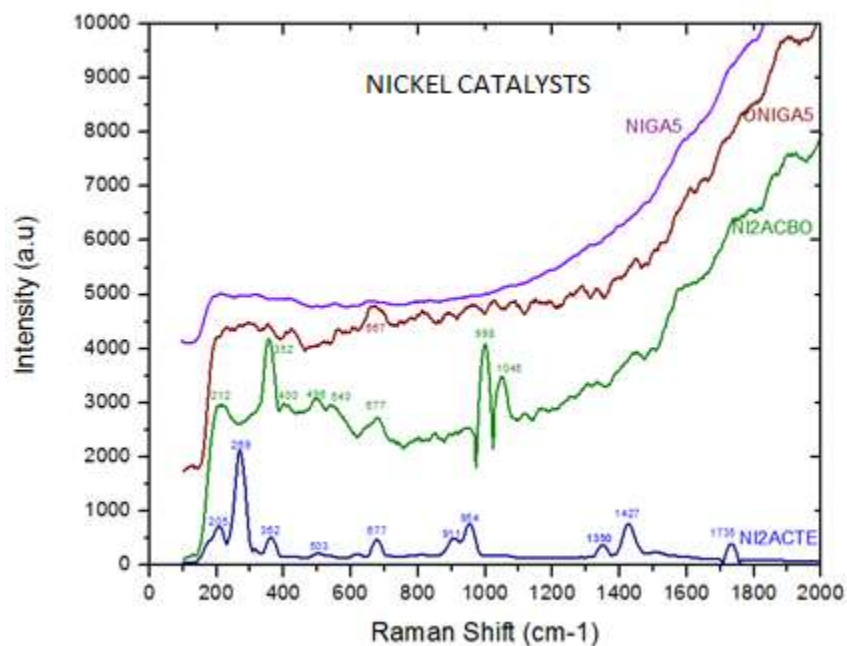


Figure. 1. Monitoring process of preparing Nickel catalysts on γ -Al₂O₃ by Raman spectroscopy.

In Figure 2, the patterns of X-ray diffraction of the catalysts of Nickel deposited on gamma alumina with 3% by weight (ONIGA3 display), reflection in 2θ of 32.6° is observed, 37.2° , 39.8° , 46.25° and 67.1° which are characteristic of the gamma phase alumina (GA). But an indication of the presence of metal particles of Ni was reflected in the sharp reflections at 2θ of 39.8° and 46.25° and increasing the intensity of the reflections of the gamma alumina phase.



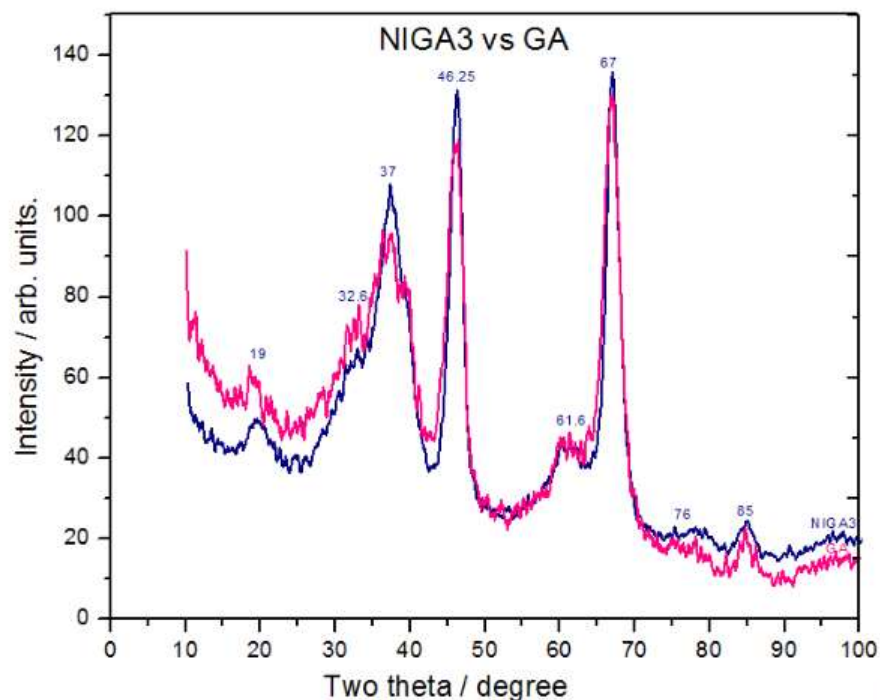


Figure 2. Patterns XRD Nickel catalyst on γ -Al₂O₃ with 3 wt% (ONIGA3) and γ -Al₂O₃ catalyst support (GA).

In figure 3 the image of scanning electron microscopy of Nickel catalysts deposited on gamma alumina with 3% by weight is shown, are achieved see crystals or clusters ranging in size from nanoscale to 7 μ m.

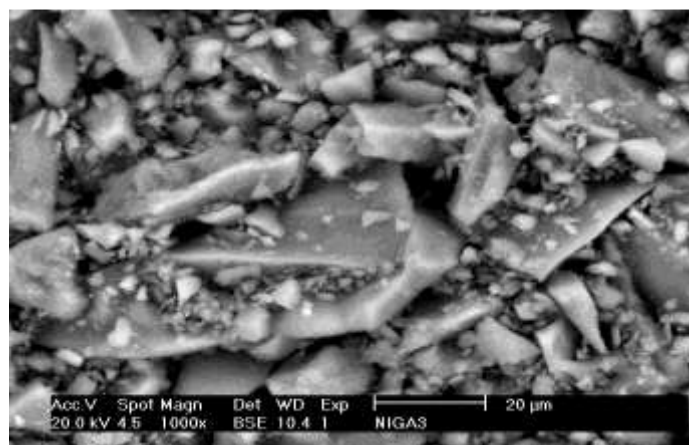


Figure 3. Image of scanning electron microscopy of Nickel catalysts deposited on gamma alumina with 3% by weight of active phase.

Table 1 shows the percentages by weight and the catalyst atomic percentage of platinum deposited on gamma alumina with 3% by weight of active phase, the data show that the amounts of reactants mixed and the preparation process of the catalysts was appropriate.

Table. 1. Average chemical composition by EDS for the nickel catalyst deposited on gamma alumina with 3% and 5% by weight of active phase.

CHEMICAL COMPOSITION OF NICKEL CATALYSTS						
Catalyst	O		Al		Ni	
	Wt %	At %	Wt %	At %	Wt %	At %
NIGA3	36.24	49.765	59.425	48.6	4.345	1.63
NIGA5	38.045	52.625	54.135	44.42	7.82	2.955



4. Summary and perspectives

With Raman spectroscopy it was found that the deposition process of the precursor salt of Nickel by the incipient wetness impregnation method was adequate, as the calcination process. By interpreting patterns of X-ray diffraction showed the presence of metal particles of Ni, and the results of chemical composition by EDS showed that the amounts of reactants mixed and the preparation process of the catalysts were suitable. With the results of characterization ensures that the catalysts will direct and accelerate the reaction hydrodeoxygenation oxygenate conversion to biodiesel and second-generation. The next stage of the project is to apply the catalysts in a reactor containing first generation biodiesel, a temperature and pressure controlled hydrogen, and evaluate the conditions under which the highest yield hydrodeoxygenation reaction occurs.

5. Acknowledgements

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6. References

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